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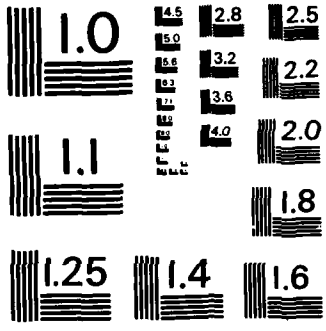

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The vaporization thermodynamics of the chromium-silicon system have been investigated in the temperature range 1300-1600K by Knudsen cell mass spectrometry. Both magnetic sector and quadrupole instruments were employed. Thermodynamic activities were obtained by direct comparison with the elements. Standard free energies of formation at 1500K, $\Delta G^\circ_f/R$ (kilokelvins) are: 1/3 $CrSi_2$, -3.07; 1/2 CrSi, -3.62; 1/8 Cr_5Si_3, -3.73; 1/4 Cr_3Si, -3.28. These data, when combined with heat capacity and entropy data from the literature, give standard enthalpies of formation at 298.15K, $\Delta H^\circ_f/R$ (kilokelvins): 1/3 $CrSi_2$, -3.36; 1/2 CrSi, -3.20; 1/8 Cr_5Si_3, -3.38; 1/4 Cr_3Si, -3.39. The $CrSi_2$ phase was found to contain the congruently vaporizing composition.

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VAPORIZATION THERMODYNAMICS OF CHROMIUM SILICIDES

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ABSTRACT

The vaporization thermodynamics of the chromium-silicon system have been investigated in the temperature range 1300-1600K by Knudsen cell mass spectrometry. Both magnetic sector and quadrupole instruments were employed. Thermodynamic activities were obtained by direct comparison with the elements. Standard free energies of formation at 1500K, $\Delta G^\circ_f/R$ (kilokelvins) are: 1/3 $CrSi_2$, -3.07; 1/2 CrSi, -3.62; 1/8 Cr_5Si_3, -3.73; 1/4 Cr_3Si, -3.28. These data, when combined with heat capacity and entropy data from the literature, give standard enthalpies of formation at 298.15K, $\Delta H^\circ_f/R$ (kilokelvins): 1/3 $CrSi_2$, -3.36; 1/2 CrSi, -3.20; 1/8 Cr_5Si_3, -3.38; 1/4 Cr_3Si, -3.39. The $CrSi_2$ phase was found to contain the congruently vaporizing composition.

INTRODUCTION

The chromium-silicon system is of technological interest because of the corrosion resistance of the chromium silicides and the potential applications of the silicides within the electronics industry. Their cohesive energies may also be used, together with those of other silicides and related species, to assess factors affecting the strengths of chemical bonds in these compounds. The early work on the chromium-silicon system has been reviewed by Chart (1) whose phase diagram is presented in Figure 1. The species identified (2) in the chromium-silicon system are Cr_3Si (which exhibits a significant range of homogeneity), Cr_5Si_3, CrSi, and $CrSi_2$ (which also exhibits a homogeneity range). Previous investigations have included combustion calorimetry (3), EMF studies using a fused salt

electrolyte (4), effusion vapor pressure experiments on the liquid in the silicon-rich part of the system (5) and effusion studies of the decomposition (6) of $Cr_3Si(s)$. More recently (1), the reaction between the respective silicides and $SiO_2(s)$ giving SiO(g) was also studied by the effusion method. None of these vapor pressure studies used mass spectrometry to confirm the presumed composition of the vapor. Furthermore, the several published results do not show very good agreement. Hence a mass spectrometric investigation of the system was undertaken.

EXPERIMENTAL

The samples were prepared by arc melting weighed mixtures of the chromium (99.99+ wt%) and silicon (99.999+ wt%) under argon and were characterized by X-ray powder diffraction. The prepared samples and residues from various experiments were further characterized by chemical analysis. Chromium content was determined by an oxidation-reduction technique. After the sample was dissolved in cold HF/HCl, the solution was treated with concentrated sulfuric acid and was evaporated until sulfur trioxide fumes were observed. Following dilution of the sample the chromium was oxidized to the +6 state by a persulfate/silver nitrate mixture; the unreacted persulfate was removed by boiling. Excess ferrous iron was added to react with chromium, and the remaining ferrous ion was back-titrated with permanganate. The spectrometric determination of silicon employed the inductively coupled plasma (ICP) technique. These results agreed closely with the compositions inferred from the original weights of the chromium and silicon.

Two sets of mass spectrometry experiments were performed. The primary set of experiments (at SUNY-Binghamton) made used of a 90° sector, single focusing, high resolution magnetic deflection instrument (Nuclide Corporation). The cell orifice was located in the center of the cell lid in these experiments. The sample was placed in a tungsten metal cup which was positioned in a tungsten Knudsen cell. The cell was heated by radiation from a tungsten helix resistance heating element surrounded by a tungsten and tantalum radiation shield assembly. The entire shield and furnace assembly was contained within a water cooled vacuum enclosure. The temperature was measured using a tungsten-rhenium thermocouple inserted into the base of the Knudsen cell; the thermocouple was calibrated with an optical pyrometer sighted into the interior of the cell. Appropriate corrections were made for the light absorbed by

the prism and window assembly. The pyrometer had a certificate of calibration traceability to the U. S. National Bureau of Standards, and its calibration was checked against the melting point of gold. The mass spectrometer was designed in such a manner that the molecular beam from the Knudsen cell, the path of the ionizing electrons and the path of the resultant ions were mutually perpendicular. To minimize the effect of mass 28 background the silicon signals were obtained with ionizing electron energies of 12.5 eV. An ionizing energy of 30.0 eV was used to obtain the chromium signal.

In the other set of experiments (at IBM-Research) a quadrupole mass spectrometer (Extranuclear Corporation) was employed. The cell orifice was located on the upper cylindrical wall of the cell used in these experiments. The sample was placed in a tungsten metal cup which was positioned in a tungsten Knudsen cell. The cell was heated using a tungsten mesh resistance furnace surrounded by a tungsten and tantalum radiation shield assembly. Again, the entire shield and furnace assembly was contained within a water cooled vacuum enclosure. The temperature was measured using a tungsten-rhenium thermocouple inserted into the base of the Knudsen cell. The calibration of the thermocouple was checked periodically against the melting point of a gold standard. As with the magnetic sector instrument, the molecular, electron, and ion beams were mutually perpendicular. Again, to minimize the effect of mass 28 background the silicon signals were obtained with ionizing electron energies of 12.5 eV. Since the chromium and silicon were measured within the same mass spectral run an ionizing energy of 12.5 eV was also used to obtain the chromium signal.

In another group of experiments, samples in open tungsten cups were heated in an induction vacuum furnace in the temperature range 1648-1663 K for for periods of 30-40 hours to examine compositional changes induced by vaporization. These compositional changes were determined by chemical analysis and confirmed by x-ray diffraction.

RESULTS

Thermodynamic activities relative to the pure solid elements were obtained as follows. The partial pressure of a species in a Knudsen cell-mass spectrometry experiment is proportional to IT, where I is the ion current due to that species and T is the temperature of the effusing vapor. Hence the thermodynamic activity of a species in the sample is given by $a = I/I^{\circ}$, where I is measured for the element

above the sample and I° is measured above the pure element under the same experimental conditions of temperature, orifice area, and electron energy (7). Although I and I° are measured in different experiments, the mass spectrometer is sufficiently stable that reproducible results are obtained. In practice, activities at a given temperature were calculated from slopes and intercepts of log IT and log I°T vs 1/T plots (see Figure 2):

$$\log a_i = (A_i - A_i^\circ)/T + (B_i - B_i^\circ)$$

where A_i and A_i° are the slopes and B_i and B_i° are the intercepts of log IT vs 1/T plots for the sample and pure element respectively. The experimentally determined A and B parameters obtained with the magnetic sector instrument are given in Table 1, and a plot of log activity as a function of composition at 1500K is given in Figure 3. A single chromium activity determination obtained with the quadrupole instrument is plotted within the CrSi-$CrSi_2$ two-phase region. Agreement with the magnetic sector results is quite good. The silicon and chromium activities in the two-phase regions were used to calculate the free energies of phase formation at 1500K:

$$(1-x)Cr(s) + xSi(s) = Cr_{1-x}Si_x(s)$$

$$\Delta G_f^\circ/R = 2.303\ T\ \text{Log}\ a_{Cr}^{(1-x)} a_{Si}^{x}$$

where x is the atom fraction of Si in one of the two single phases. Free energy functions, $\Phi' = -(G^\circ_T - H^\circ_{298.15})/T$, were evaluated from published thermodynamic data. Entropy and heat capacity data for the silicides were taken from the data of Kalishevich and coworkers (8,9) for $CrSi_2$, CrSi, and Cr_5Si_3. For Cr_3Si, the entropy was taken from Kalishevich and coworkers (8) and the high temperature heat capacity expression from Golutvin and Chin-K'uei (3). Since the latter's measurements on Cr_3Si and the other silicides of chromium did not extend above 900K, their expression for Cr_3Si was adjusted in a manner which, when applied to their results for the other chromium silicides, brings the calculated free energy functions for those silicides into agreement with free energy functions calculated from the data of Kalishevich and coworkers (8,9). It should be noted that the resulting free energy functions for Cr_3Si are virtually identical to those obtained by assuming the high temperature heat capacity of Cr_3Si to be additive of the solid elements (1). Thermodynamic data for elemental silicon (10) and chromium (11) were taken from the JANAF Tables. Enthalpies of phase formation were calculated from the free energies at 1500K by use of the relation,

$$\Delta H^\circ_{298.15} = \Delta G^\circ_T + T\Delta\Phi'$$

The free energy and enthalpy of formation results are given in Table 2. The data published by Chart (1) are included for comparison; agreement is acceptable.

For the samples heated in vacuum for extended periods it was found that samples richer in Cr than $CrSi_2$ lost Cr preferentially, and the samples richer in Si than $CrSi_2$ lost Si preferentially. Hence the samples move toward a congruently vaporizing composition within the $CrSi_2$ single-phase region. A schematic pressure vs composition diagram at 1500K is given in Figure 4. The Cr-Si system may be compared with the V-Si and Mn-Si systems in this connection. Because of the high relative volatility of Mn, there is no congruently vaporizing composition within the Mn-Si system (12); Mn is lost preferentially at all compositions. However, in the V-Si system (7), in which vanadium is relatively less volatile than silicon, there are two congruently vaporizing compositions. At about 1900K and below, V_3Si contains the congruently vaporizing composition, and at 2050K and above V_5Si_3 is congruently vaporizing. Within some range of temperatures between 1900K and 2050K, both phases will exhibit a convergent congruently vaporizing composition, and there will be a divergent congruently vaporizing or euatmotic composition within the two-phase region.

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REFERENCES

1. T. G. Chart, Met. Sci., **9**, 504 (1975).

2. H. J. Goldschmidt and J. A. Brand, J. Less-Common Metals, **3**, 34 (1961).

3. Yu. M. Golutvin and L. Chin-k'uei, Russ. J. Phys. Chem., **35**, 62 (1961).

4. V. N. Eremenko, G. M. Lukashenko, V. R. Sidorko, and A. M. Khar'kova, Sov. Powder Metall. Met. Ceram., **1971**, 563.

5. J.-P. Riegert, A. Vermande, and I. Ansara, High Temp.-High Pressures, **5**, 231 (1973).

6. A. S. Bolgar, S. P. Gordienko, A. A. Lysenko, and V. V. Fesenko, Russ. J .Phys. Chem., **45**, 1154 (1971).

7. E. K. Storms and C. E. Myers, High Temp.Sci., **20**, 87 (1985).

8. G. I. Kalishevich, P. V. Gel'd, and R. P. Krentsis, Russ. J. Phys. Chem., **12**, 1602 (1965).

9. G. I. Kalishevich, P. V. Gel'd, and R. P. Krentsis, High Temp. (USSR), **4**, 613 (1966).

10. D. R. Stull and H. Prophet, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. No. 37 (1971).

11. M. W. Chase, J. L. Curnutt, H. Prophet, R. A. McDonald, and A. N. Syverud, J. Phys. Chem. Ref. Data, **4**, 1 (1975).

12. H. Nowotny, J. Tomiska, L. Erdelyi, and A. Neckel, Monats. Chem., **108**, 7 (1977).

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Table 1

ACTIVITY PARAMETERS FOR TWO-PHASE REGIONS: Cr-Si SYSTEM

$$\log a_i = (A_i - A^\circ_i)/T + (B_i - B^\circ_i)$$

Two-Phase Region	$(A-A^\circ)_{Cr}$	$(B-B^\circ)_{Cr}$	$(A-A^\circ)_{Si}$	$(B-B^\circ)_{Si}$
Cr_3Si-Cr_5Si_3	-1702	0.401	-526	-1.356
Cr_5Si_3-CrSi	-3241	0.772	-1748	0.483
CrSi-$CrSi_2$	-1882	-0.348	-2815	1.344
$CrSi_2$-Si	1493	-3.484	1027	-0.715

Table 2

STABILITY DATA FOR CHROMIUM SILICIDES (kilokelvins)

Compound	Region	$\Delta G^\circ_f/R$ (1500K)	$\Delta H^\circ_f/R$ (298.15K)	Notes
1/4 Cr_3Si(s)	3/1-5/3	-3.28	-3.39 +/-0.2	(1)
			-3.18	(3)
1/8 Cr_5Si_3(s)	3/1-5/3	-3.64	-3.29	(1)
	5/3-1/1	-3.82	-3.46	(1)
			-3.38+/-0.2	(2)
			-3.36	(3)
1/2 CrSi(s)	5/3-1/1	-3.55	-3.14	(1)
	1/1-1/2	-3.68	-3.27	(1)
			-3.20+/-0.2	(2)
			-3.30	(3)
1/3 $CrSi_2$(s)	1/1-1/2	-3.07	-3.36+/-0.2	(1)
			-3.21	(3)

Notes:
(1) This work, magnetic sector instrument
(2) Mean value, this work
(3) Reference 1

LIST OF FIGURES

1. Chromium-Silicon Phase Diagram: after Chart (1)

2. Log IT *vs.* 1/T

   Typical data: a = Si, element; b = Si, sample

   c = Cr, element; d = Cr, sample

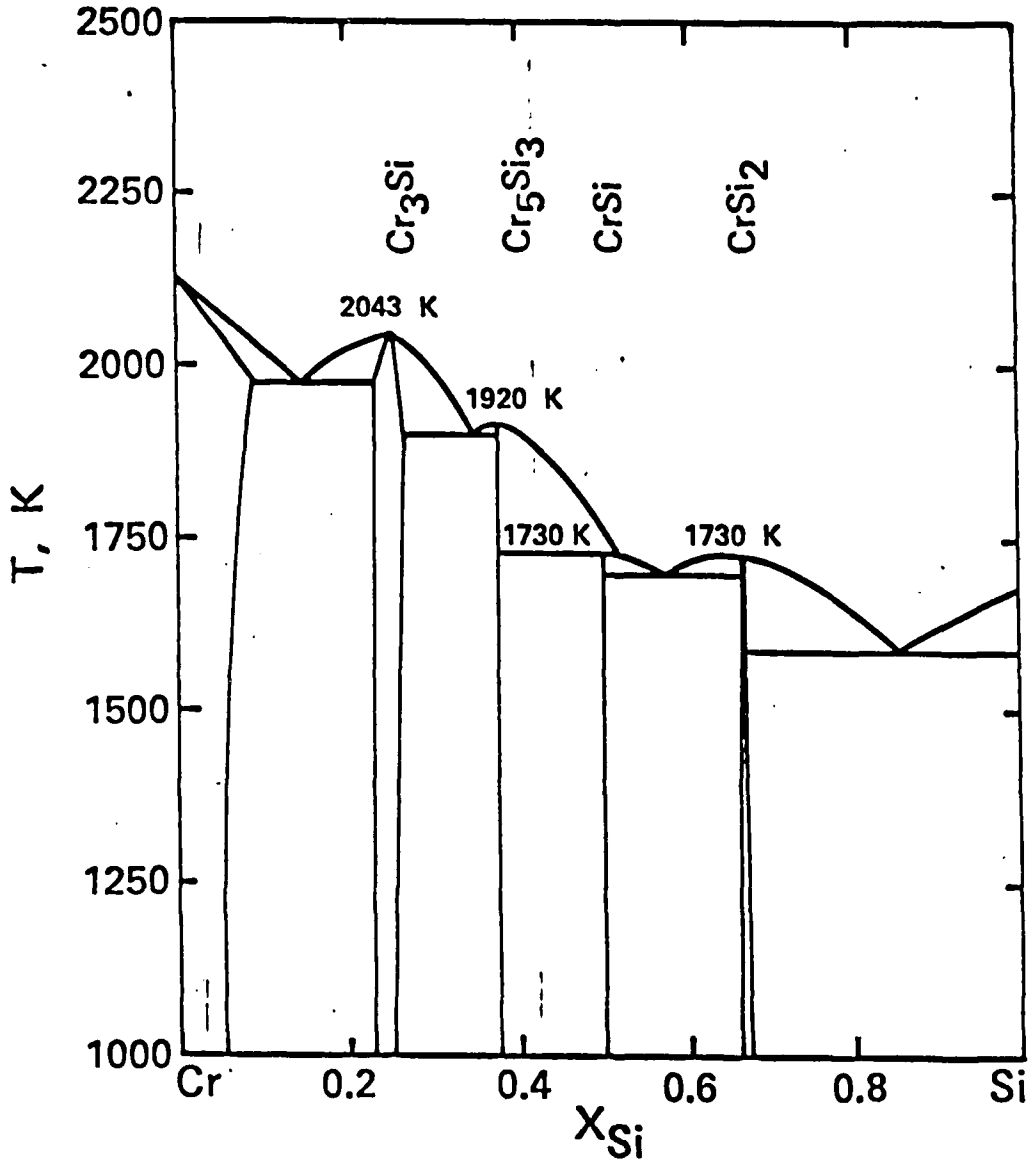
3. Log Activity *vs.* Composition at 1500K

   x = Cr (magnetic sector)
   * = Cr (quadrupole)
   o = Si (magnetic sector)

4. Pressure *vs.* Composition at 1500K (schematic)

INDEX ENTRIES

Chromium silicides, Cr_3Si, Cr_5Si_3, CrSi, $CrSi_2$, vaporization behavior, vaporization thermodynamics, activities, free energy of formation, enthalpy of formation, congruent vaporization, Knudsen effusion, mass spectrometry.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2250
2000
1750
1500
1250
1000
T, K
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0.4
0.6
0.8
Si
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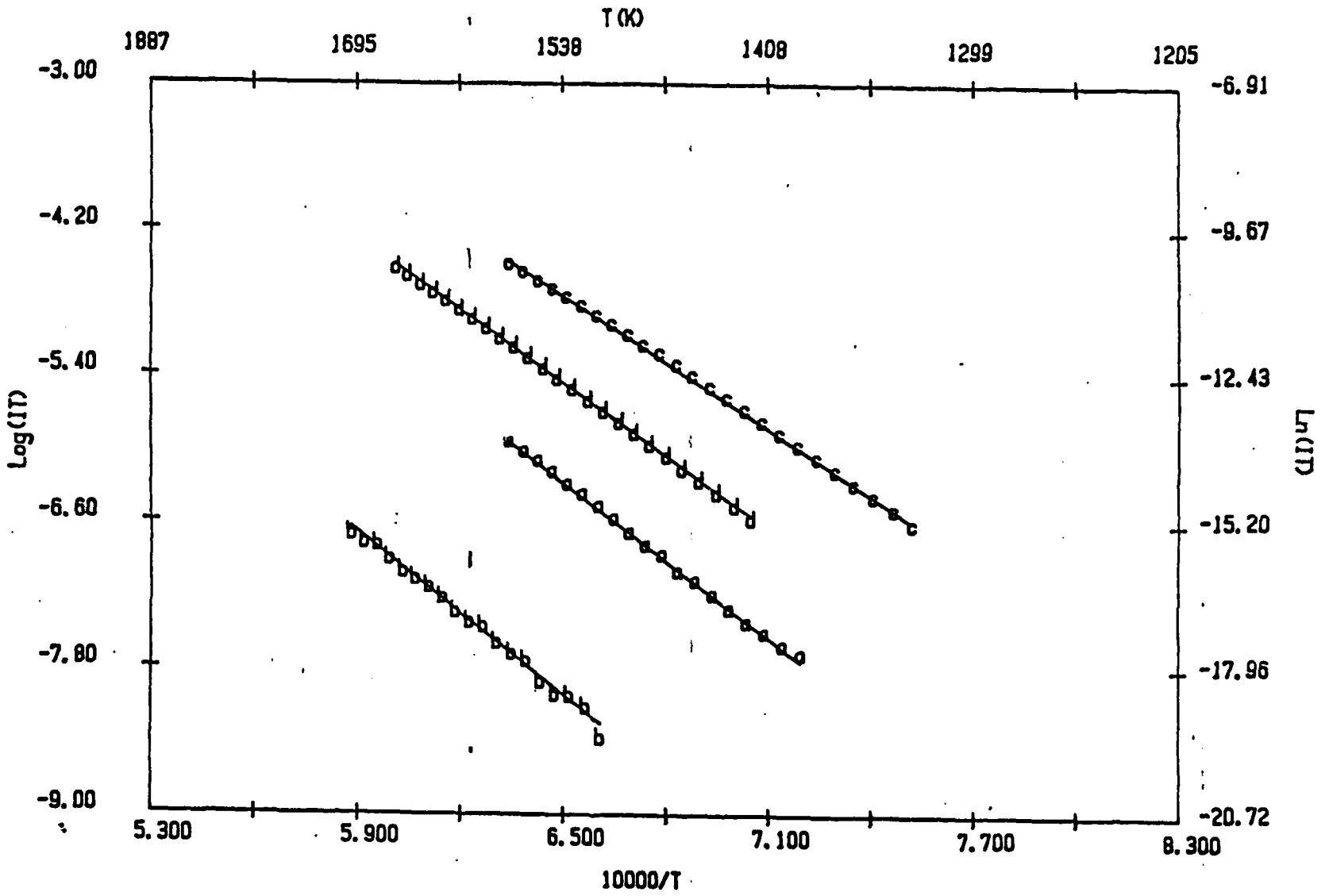
Cr_3Si
Cr_5Si_3
CrSi
$CrSi_2$
2043 K
1920 K
1730 K
1730 K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1538
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-9.00
Log(IT)
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-9.67
-12.43
-15.20
-17.96
-20.72
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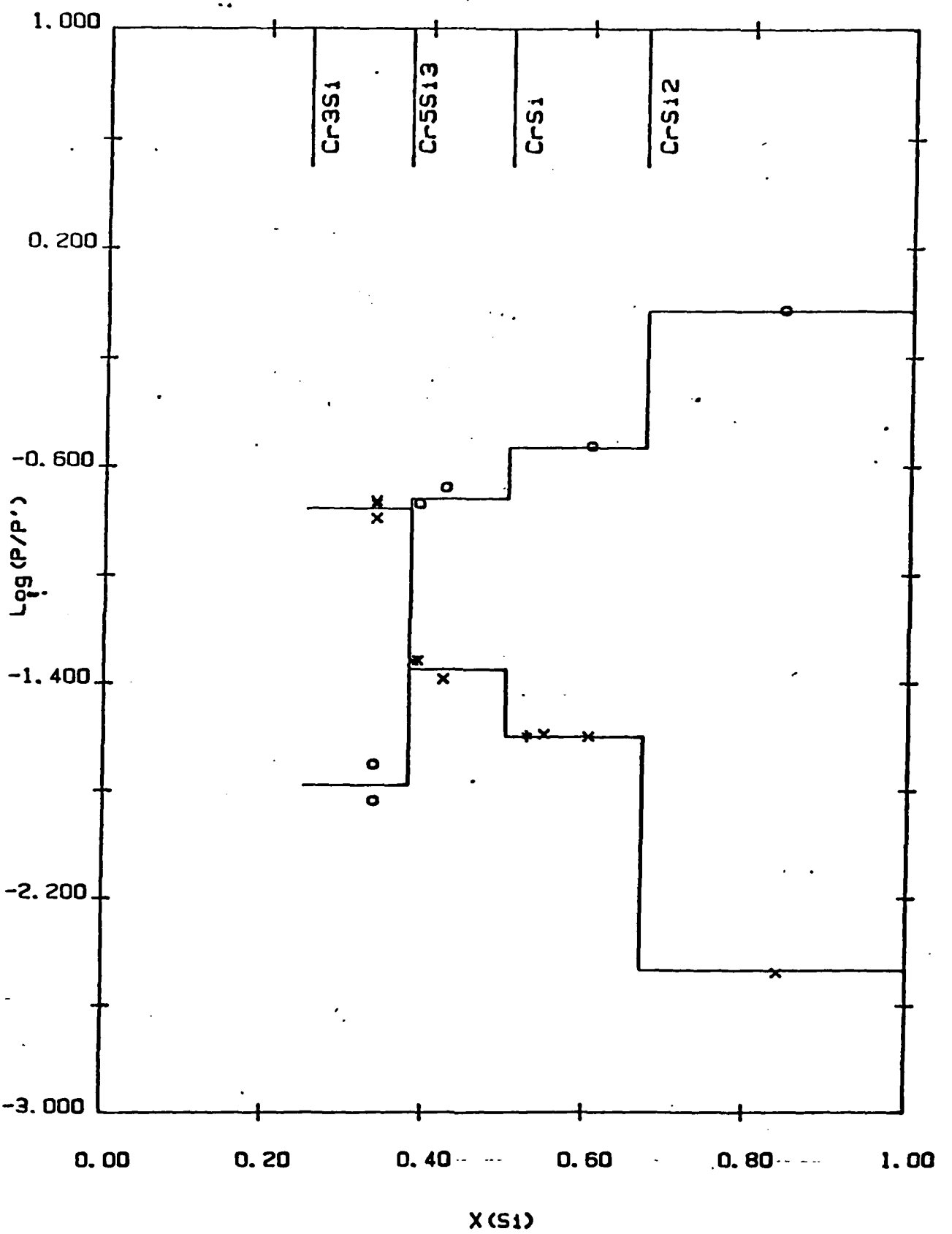
b
c
d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Log (P/P')
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Cr5Si3
CrSi
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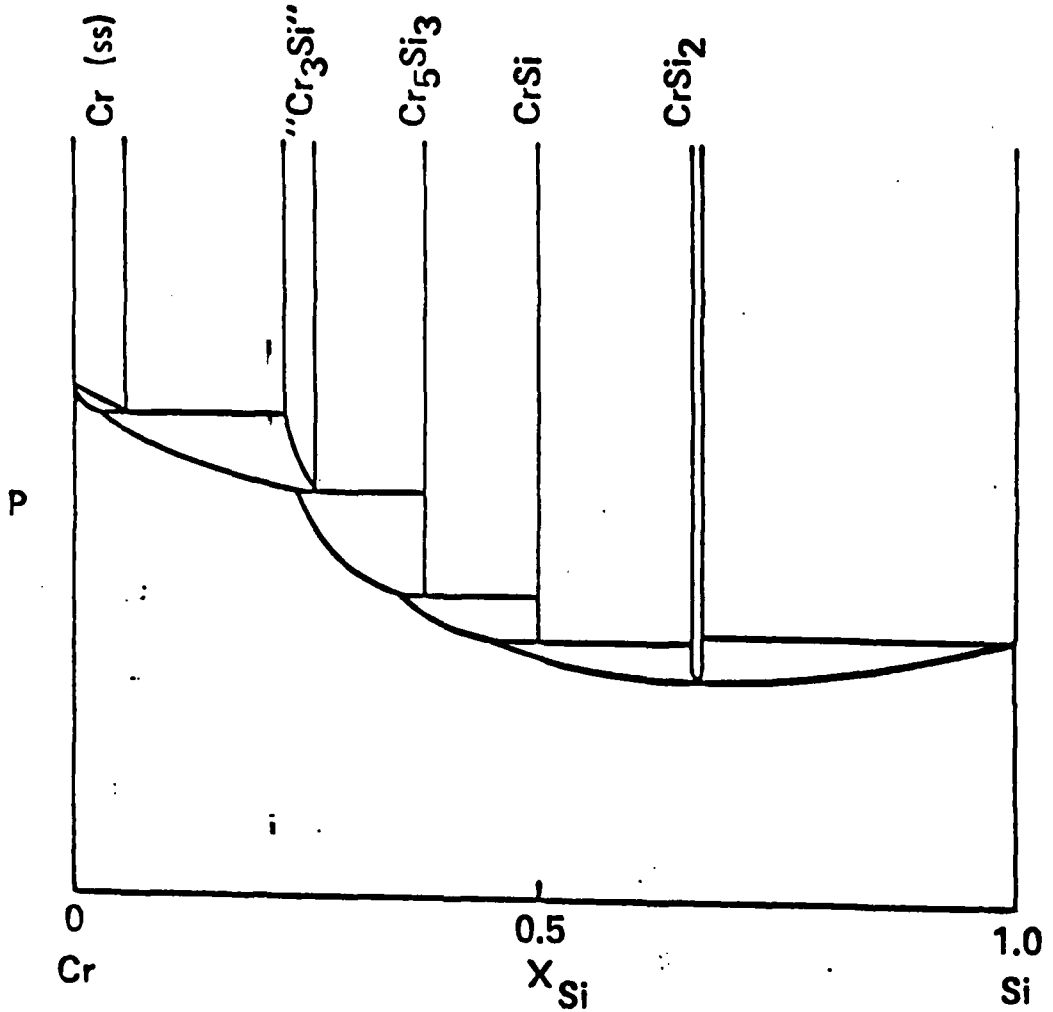
0.40
0.60
0.80
1.00
X(Si)



Cr–Si SYSTEM 1500K

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